THESIS

MODELING STRONTIUM-90 TRANSPORT AND POTENTIAL REMEDIATION FROM A CONTAMINATED AQUIFER

Submitted by

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ABSTRACT

MODELING STRONTIUM-90 TRANSPORT AND POTENTIAL REMEDIATION FROM A CONTAMINATED AQUIFER

Radioactive waste injected into depleted oil reservoirs runs the risk of contaminating local aquifers if the bore casing of the injection hole were to fail. The currently proposed method of remediation involves multiple iterations of flushing to remove all contaminants. This is inefficient as the radionuclides adsorb into the aquifer rock and desorb back into the water table after a period of time. The adsorption/desorption kinetics for the activity concentration in the injection solution have been transformed into first order rate equations to model the interactions over time. The adsorption of Sr-90 has been modeled as a competitive process between two categories of rock.

In parallel, almond hulls have been proposed as potential biosorbents for Sr-90. The kinetics have also been modeled into first order equations. This study quantifies how the addition of the almond hull kinetics will affect the activity concentration in the injection solution and within the two rock types. It simulates how the addition of an almond hull biosorbent into the injection solution would immobilize the radionuclides reducing the activity in the surrounding rock. With the biosorbent added to the system, the activity concentration in the injection solution is 39% of the activity concentration without by the 10^{th} day. It was found that there was an 62% reduction in the total activity concentration in Rock Type 1 and Rock Type 2 after 10 days compared to adsorption using no biosorbent.

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CHAPTER 1 – INTRODUCTION

The objective of this project is to model the radiation transport within an unintentionally contaminated aquifer from the injection of radioactive waste. According to I. V. Tokorev et al, 2007, “The disposal into the geological space appears to be the best way to ensure the safety in the management of liquid radioactive waste” (Tokarev, 2009). There are potential hazards associated with this disposal method. An injection well used in the disposal of this liquid radioactive waste can intersect both the repository formation used for the disposal of these radioactive waste materials and a potable aquifer. Any failure in the well can result in the contamination of the potable aquifer.

Typically, with any injection or fluid disposal well, fluids are injected into a selected geologic formation having sufficiently high flow capacity (permeability) and high storage capacity (porosity) to act as a long-term repository for these fluids. Injection/disposal wells used for the disposal of waste materials have already been widely adopted within several industries utilizing this technology (McCurdy, 2005). The oil industry commonly disposes of unwanted formation brine produced in conjunction with the hydrocarbons by re-injecting the produced water into wastewater injection wells. Injection of waste materials has also been used by the chemical industry to dispose of waste materials that would otherwise pose an environmental hazard if stored open on the surface (McCurdy, 2005).

The disposal of radioactive waste into injection/disposal wells has already begun in Russia (Rumynin, 2005). There are currently two wastewater injection wells in Western Siberia disposing of Low-Level Waste and Intermediate Level Waste (Rumynin, 2005). Any disposal or injection well runs the risk of potentially contaminating local aquifers

intersected by the borehole if the casing integrity or the cement bond interface along the casing and/or at the borehole wall were to fail and allow for these waste materials to enter the aquifer. This potential environmental hazard was the motive for a study conducted by V.G. Rumynin et al., 2005 from the Institute of Environmental Geology of the Russian Academy of Sciences.

Rumynin cited flushing as a potential remediation solution for the aquifer. In situ flushing involves flooding the aquifer and displacing the contaminated injection solution near the proximity of an extraction well where it can be removed (Lee & Zhai, 2007). The study found that if the integrity of the borehole were to fail, and some of the wastewaters were to enter an aquifer, then even with multiple iterations of flushing of the polluted aquifer, the adsorption of radionuclides within the aquifer may be irreversible (Rumynin, 2005). Sr-90 in the injection solution was found to be adsorbed into the rock of the aquifer. The study found that 15-20% of the Sr-90 activity is retained in the rock samples after four cycles of flushing with either of fresh water or a sodium nitrate solution.

The retained Sr-90 in the aquifer would not be a concern if it was immobile and permanently adsorbed into the aquifer rock. Once the Sr-90 is adsorbed into the aquifer system, it is the desorption back into the groundwater that poses the greatest hazard. Rumyin's study conducted four simulated iterations of flushing of an aquifer and found that each subsequent flush showed a continuous release of radionuclides back into the injection solution.

Rumynin conducted batch experiments on sedimentary rock samples that represented a potentially contaminated aquifer. These resultant data provided sorption isotherms to model the adsorption effects of injected radioactive waste into the system and the desorption affects through subsequent flushing to mitigate the radioactive waste contamination. From the isotherm data, a simulation model was created to describe the exchange of radionuclides between the injection fluid and the rock surface within the aquifer. The exchange of radionuclides was modeled to be a competitive process between two types of minerals, based on relative surface areas, which compose the porous and permeable aquifer that was contaminated within the well and the injected waste:

- Typical minerals that make up the primary grain volume such as Quartz, Carbonate Rock and Feldspars
- Mostly Clay and micaceous type minerals like Illite and Smectite that have high Surface to Volume ratios

When the simulated injection solution was introduced to the rock composite, the strontium ions were adsorbed onto one of the two rock type surfaces resulting in the decrease in the injection solution activity concentration. The adsorption of radionuclides into the rock results in the desorption of radionuclides from the injection solution.

The March 11, 2011 the nuclear accident at the Fukushima Daiichi nuclear energy plant has driven researchers to investigate adsorbent materials for radionuclides. These adsorbent materials have been used to sequester the radioactive contamination (Parab, 2013; Shibata, 2016; Abdelkareem, 2012). These sources have specifically focused on using agriculture waste products as potential adsorbent materials. One readily available

proposed adsorbent material is green almond hull, a waste generated from the production of almonds (Ahmadpour, 2010). The annual production of almonds (shelled) is projected to be 1.3 million tons worldwide (United States Department of Agriculture, 2017). The kernel of the almond composes only 14% of the total weight of the fruit, with 53% of the weight coming from the hull and 33% from the shell (Godini, 1983). This would generate around 5 million tons of almond hull that is generally considered useless (Godini, 1983). Almond hull cannot be consumed by animals and are usually disposed of through burning (Ahmadpour, 2010). These factors make almond hull a great prospect for a radionuclide adsorbent.

The thesis will address the question of whether a biosorbent within the injection solution could immobilize the Sr-90 ions therefore reducing the available Sr-90 ions for adsorption into the surrounding rock. The goal of this thesis is to quantify the effects of the introduction of a third adsorption process, a biosorbent, into Rumynin's model. This model simulates the addition of a biosorbent into the injection fluid to compete with high/low relative surface area type minerals for the adsorption of radionuclides. First, the concentration of Sr-90 in the injection fluid and the surrounding rock is modeled and compared to Rumynin's results, and then the biosorbent is introduced and quantified.

CHAPTER 2 – LITERATURE REVIEW

2.1 Defining a Deep-Injection Well

An injection well must have the proper geologic characteristics to store hazardous waste. The well must be of a porous media with adjacent impervious rock, or what is called seal rock, above and below the waste repository to contain the fluids to only the porous rock media that is receiving the injected radioactive waste. The seal rock would normally be composed of a shale or anhydrite type materials to form a complete seal that is impermeable to the flow of fluid and ductile or plastic enough under in situ pressure/temperature to have the ability to self-heal in case these seals have been pierced by natural occurring fracturing or faulting. If not, the faults or fractures could breach these impermeable layers and provide additional pathways for the waste fluids to move. Any lack of containment of the injected radioactive waste to just the intended injection formation would jeopardize the rationality of a disposal repository well concept. In this geologic setting the porous media can act as a large-scale storage repository for the disposal and storage of hazardous waste. Please see Figure 1 for an ideal setting for a useful radioactive waste injection well.

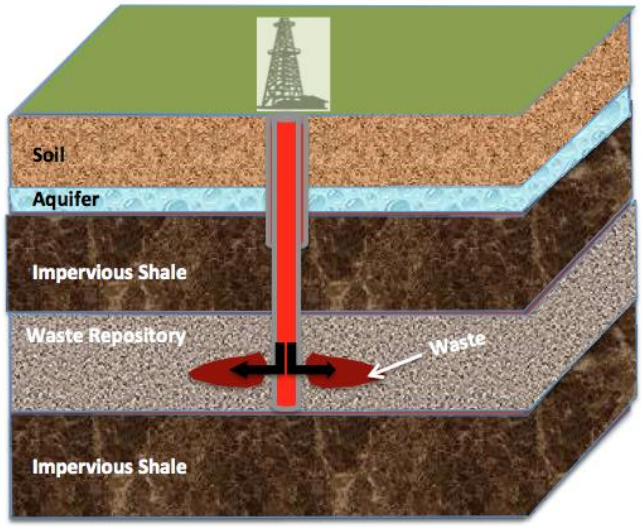

Figure 1: Ideal Geologic Setting for a Radioactive Waste Disposal Well

Almost all wells drilled into the earth rely on a series of concentric pipe or casing to add structural stability to the borehole, eliminating the chance of the borehole wall collapsing or caving and isolating the various permeable intervals intersected by the physical drilling of the wells. To ensure the isolation of each layer, the casing is typically cemented into the borehole where cement is pumped down the casing string and up the annular space surrounding the casing. This is a critical step in preparation of any drill hole and this annular space must be cemented properly to prevent the flow of fluids around the annulus of the casing causing unintended injection fluids to enter into other geologic formations, which could be a potable aquifer. The cement must not only bond with the iron casing strings of pipe, but also the cement must bond to the borehole wall which is composed of various naturally occurring geologic materials. In drilling the well, there can also be borehole washouts and irregularities found along the surface of the wellbore that must also be filled with cement and bonded to this irregular borehole surface. Finally, in addition

to the normal casing, there can sometimes be an injection string of tubing or the innermost casing string that is used in place of injection tubing. This innermost string of pipe is used to transport the injection fluid down the wellbore and out into to the desired liquid waste repository formation through perforations at the preferred injection site in the wellbore. The casing is perforated at the repository level in the well to allow the injection string to communicate with the repository formation and allow the flow of radioactive waste into the repository. The injection tubing must also be non-reactive with any injection fluids.

If for any reason the casing is parted, corroded or there is poor cement bond along the casing or wellbore, then the injection materials can move along these defects and enter into other geologic formations intersected by the wellbore which could be other permeable formations or even a potable aquifer which this study simulates.

2.2 Strontium Adsorption

A conceptual model of liquid-solid interface can be used to explain the mechanisms controlling the adsorption of radionuclides within an injection well. The Electrical Double layer describes the transport of charged ions across the interface between two phases of matter. In this case it is the interface between the aquifer wall and the injection/flushing solution.

Clay minerals with large surface areas tend to develop an excess negative charge on the surface (White, 2006). When the charged surface of the aquifer walls interacts with a solution containing charged ions, the injection fluid, the electrostatic potential attracts positive ions along the surface of the clays. (University of Cambridge, 2017). This results in two layers of charge forming the electrical double layer (EDL) (University of Cambridge,

2017). Past the EDL, the electrostatic potential creates a diffuse distribution of charges. The distribution of cations and anions are illustrated in Figure 2 below:

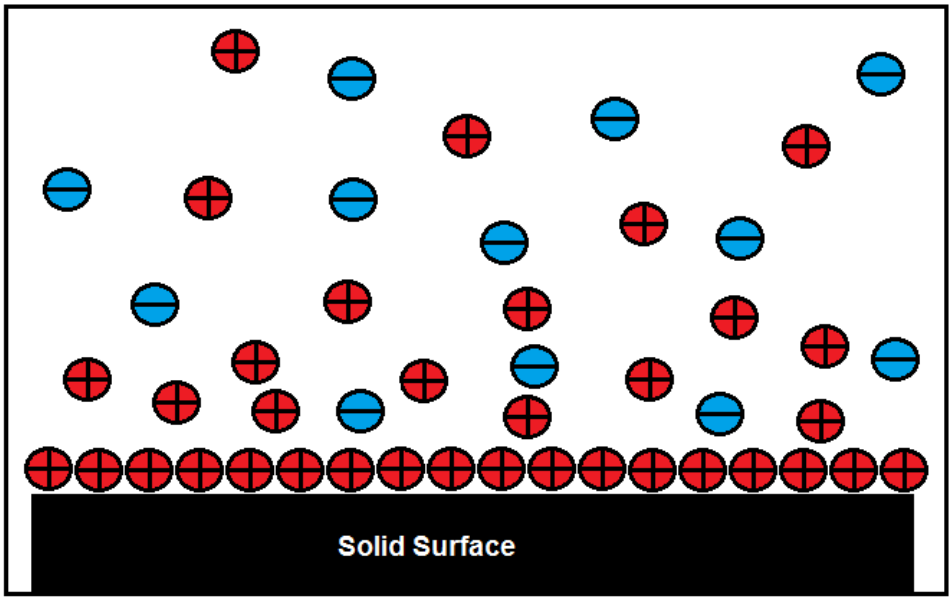

Figure 2: Illustration of Ion Distribution in Liquid-Solid Interface

The adsorption is also subject to Brownian motion that contributes to the exchange of ions. Brownian motion is the random movement of atoms or molecules within a fluid (Syed, 2013). As fluid is injected into the porous media, the system is constantly being disturbed. Brownian motion perturbs the system and affects the charge density of ions. The number density of positive ions is less when Brownian motion is taken into account. This changes the potential and the relative permittivity of the cations in the fluid. Brownian motion was found to be an important driving mechanism for cation exchange.

2.3 Quantifying Adsorption Radionuclides

The Electrical Double Layer model provides a physical mechanism for adsorption of ionic species, but the exchange mechanism has been quantified with theory for homogenous samples of a single elemental composition (Kitamura A.). Most rock samples found in nature are composed of multiple types of minerals of different binding sites that the theory cannot quantify. This requires the characterization of these interactions to rely on empirical means. These interactions are characterized by adsorption isotherms. An adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. These isotherms are determined experimentally in the lab. The isotherm curves are characterized using a range of well-defined set of temperatures and pressures.

The adsorption isotherm used in the Rumynin study was the Freundlich Isotherm, represented through the following equation:

$$N^s = K_F^s C^{n^s} \quad \textbf{(1)}$$

Where:

N^s is the activity concentration in a solid surface $(\mathrm{Bq}\ cm^{-3})$

C is the activity concentration in the solution $(\mathrm{Bq}\ cm^{-3})$

K_F^s is the Linear Freundlich Constant $(\frac{\mathrm{Bq}}{cm^3_{Rock}})(\frac{cm^3_{Solution}}{Bq})$

n^s is the Exponential Freundlich Constant

The superscript s is used to denote the adsorption step

The Freundlich Isotherm is an empirical equation to relate the exchange of cations between a liquid and a solid. The Freundlich constants are determined empirically based on the experimental data. The activity concentration in the injection solution as a function of the activity concentration in the rock on a log-log graph. The Freundlich constants are calculated by taking a linear fit of this data. The units of the Exponential Freundlich constant is unitless and is necessary to cause the isotherm to curve, becoming less steep at higher concentration. The Linear Freundlich Constant acts to convert the equation from units of $\frac{Bq}{cm^3}$ in the injection solution to $\frac{Bq}{cm^3}$ in the surrounding rock.

The concentration of Sr-90 in the solid surface is plotted as a function of the solution concentration. Being empirical in nature, it is the desired isotherm for modeling heterogeneous media. The other common isotherm, the Langmuir isotherm, assumes a homogenous solid interface where each sorption site is identical (Seungman, 2005). Thus, the Freundlich isotherm is common for a heterogeneous surface (Dada, 2012).

2.4 Strontium Contamination modeling in Aquifer

Rumynin's study simulated the injection of radioactive waste into aquifer type mineralogy with subsequent flushing stages through a batch study that incubated rock samples in their corresponding flushing liquids. The rock sample was initially incubated in a radioactive waste fluid to simulate the contamination of the aquifer. Then the contaminated samples were incubated in different flushing fluids to represent various scenarios attempting to flush the contaminants from the aquifer.

The mineral composition of Rumynin's samples was determined by measuring the mineral composition of rock sampled from an aquifer that could potentially be

contaminated from the injection of radioactive waste. Table 1 shows the composition of the "average sample" that was used in his study.

Table 1: Composition of Minerals in Each Rock Sample [Reproduced from Rumyin (2005), Table 2]

Mineralogy composition of the rock

No.	Mineral	Lab data (% mass)	Type of reactive sites
1	Plagioclase	2.6	1
2	Biotite	7.6	2
3	Hydromica	11.7	2
4	Montmorillonite	11.4	2
5	Quartz	63	1
6	Carbonates	1.1	1
7	Rutile	0.3	1
8	Pyrolusite	0	1
9	Total mass of mineral phase (g)	98.04	

These samples were initially placed in a solution containing Sr-90 and then incubated at a pre-defined temperature and pressure that would correspond to a certain depth within the well. This initial stage represented the injection of the radioactive waste that inadvertently contaminated the neighboring aquifer. The experiment then used various scenarios and combinations of sodium nitrate (10 g/L) and groundwater flushing to mitigate the situation to flush and remove the initial radioactive waste materials.

In addition, the experiment was conducted using solutions of varying activity concentrations to simulate varying concentrations of waste. The adsorption or injection stage was conducted for 9 days in his study. The activity of the injection fluid was measured using both the HPGe-MCA gamma and beta scintillation counting systems once local equilibrium was achieved. The study measured the activity concentration of the solution on daily intervals for a total of 9 days.

The flushing or desorption step was conducted by removing the radioactive waste contaminating incubated samples from the radioactive waste solution, and then placing them in the non-radioactive flushing solutions. Identical to the adsorption step, the study measured the activity concentration of the solution on daily intervals for a total of 9 days. These data were plotted and fitted to determine Isotherms for specific temperatures and pressures. The experiment was conducted for five different activity concentrations of 1.628E+07, 1.628E+06, 37000, 3700, and 370 Bq cm^{-3}.

Two isotherms were created for both the adsorption and desorption step. The activity concentration is denoted as N^s and N^d corresponding to either the adsorption or desorption step, respectively. A graph of the Freundlich Isotherms under atmospheric pressure, a temperature of 20 °C, and an initial activity concentration of 1.628E+06 Bq cm^{-3} can be seen in Figure 3:

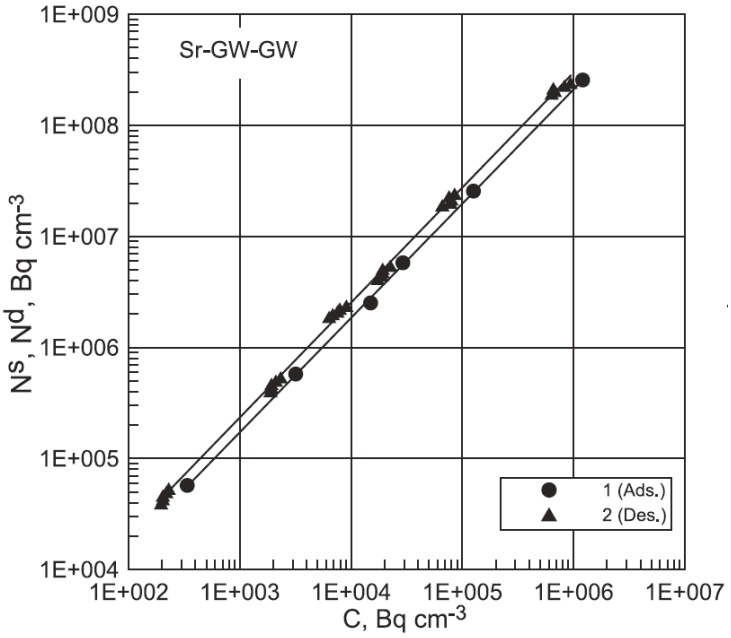

Figure 3: Adsorption Isotherm for Sr-90 Adsorption and Desorption in a Simulated Groundwater Environment (Rumynin, 2005) [Reproduced from Rumyin (2005), Fig 4]

The activity concentrations in the rock for each sorption step (N^s and N^d) are shown as a function of the activity concentration in the groundwater (C). The two stages of injection (N^s) and flushing (N^d) are characterized by different linear and exponential Freundlich constants that lead to different equilibrium conditions. These data were plotted on a log-log and a linear graph. These were constructed by fitting the data to a linear function on the log-log plot to determine the n^s and K_F^s terms.

$$\log(N^{s/d}) = n^s \log(C) + \log(K_F^{s/d}) \quad \textbf{(4)}$$

Once the Freundlich constants were determined, a simulation of the sorption kinetics was constructed from the batch data to attempt to describe the kinetics of the system. The adsorption of radionuclides in the surface of the rock was hypothesized to be a competitive process between the different mineral types having different adsorption properties. To define the system, a dual-site one-component adsorption model is used where two types of categorized rocks of different compositions compete for adsorption of

radionuclides. The first rock category represented rock that contained minerals with weak mass-exchange properties such as quartz and feldspar. The second category of rock represented rock with active mineral geosorbents such as clay and micaceous minerals. The two categories of rock differ in kinetic parameters controlling the interactions between the radionuclides and the binding sites in the rock. These parameters were optimized to best fit the batch data from the experiment.

The Freundlich Equation that relates the concentration of radionuclides in the solution to that in the different types of rock needs to be converted into a form that can be inserted into a simulation tool that will calculate the activity in the rock over time. The time derivative of the concentration of radionuclides for both types of rock in the dual site model can be expressed through the Rumynin's Kinetic Freundlich Equation (Rumynin, 2005):

$$f\frac{dN_1}{dt} = \alpha_1(K_{F_1}C(t)^{n_1} - N_1) \qquad \textbf{(5)}$$

$$(1-f)\frac{dN_2}{dt} = \alpha_2(K_{F_2}C(t)^{n_2} - N_2) \qquad \textbf{(6)}$$

Where:

K_{F_1} is the Linear Freundlich Constant for Rock Type 1 $(\frac{\text{Bq}}{cm^3_{Rock}})(\frac{cm^3_{Solution}}{Bq})$

K_{F_2} is the Linear Freundlich Constant for Rock Type 2 $(\frac{\text{Bq}}{cm^3_{Rock}})(\frac{cm^3_{Solution}}{Bq})$

n_1 is the Exponential Freundlich Constant for Rock Type 1

n_2 is the Exponential Freundlich Constant for Rock Type 2

N_1 is the activity concentration in Rock Type 1 $(\text{Bq}\ cm^{-3})$

N_2 is the activity concentration in Rock Type 2 $(\mathrm{Bq}\ cm^{-3})$

f is the percent composition of Rock Type 1

α_1 is the kinetic adsorption rate constant for Rock Type 1 (d^{-1})

α_2 is the kinetic adsorption rate constant for Rock Type 2 (d^{-1})

Because both equations are dependent upon the activity concentration of the injection solution, it is theorized that the two rocks categories interact with both the solution and with each other.

To build the dual-site model, Rumynin created certain assumptions that corresponded to the geologic composition of the rock. The problem arises in trying to create a dual-site model that models the behavior of both types of rock given that only one Linear Freundlich Constant is representative of the whole sample. The study used the following equations to relate the total Freundlich constant to those of each Rock Type:

$$N = fN_1 + (1 - f)N_2 \qquad \textbf{(7)}$$

and

$$K_F = fK_{F_1} + (1 - f)K_{F_2} \qquad \textbf{(8)}$$

Where the Linear Freundlich Constant for each Rock Type was chosen to be proportional to the amount or weight percent of each Rock Type used in the composition of the sample. Due to the general classification of each Rock Type (weak vs strong mass-exchange properties), $f$was chosen to be 75% by Rumynin to roughly match the composition of rock in a potentially contaminated aquifer.

Other assumptions were also based of the geologic composition of the sample. Rock Type 2 is defined to be the Clay and Micaceous type minerals with strong mass-exchange properties. Thus, the value of K_{F_2} was chosen to be higher than K_{F_1} such that it dominated the interaction.

A page is a list of the constants published in Rumynin's paper for Sr-90 in a groundwater solution at atmospheric pressure and 20°C is provided in table 2. These environmental parameters will be assumed for the rest of the thesis.

Table 2: Kinetic Parameters for Sr-90 in a Synthetic Groundwater Solution at 20°C and Atmospheric Pressure (Rumynin, 2005)

Parameter	Value	Units
K_F	141	$(\frac{\text{Bq}}{cm^3_{Rock}})(\frac{cm^3_{Solution}}{Bq})$
K_{F_1}	10	$(\frac{\text{Bq}}{cm^3_{Rock}})(\frac{cm^3_{Solution}}{Bq})$
K_{F_2}	532	$(\frac{\text{Bq}}{cm^3_{Rock}})(\frac{cm^3_{Solution}}{Bq})$
f	0.75	-
α_1	60	d^{-1}
α_2	60	d^{-1}

The adsorption isotherm modeled the activity concentration between the aquifer rock and the injection solution. Now that the equations relating to each rock type were configured, Rumynin needed to ensure that all the radioactivity was conserved in the system. A mass balance equation was used by Rumynin to conserve the mass of radionuclides in the system.

$$M^T = VC + \frac{m_s}{\rho_b} N \qquad \textbf{(9)}$$

where:

M^T is the total inventory of Sr-90 in the aquifer system (Bq)

V is the volume of solution (cm^3)

m_s is the mass of the sample of rock (g)

ρ_b is the bulk density of the rock $(g\ cm^{-3})$

Rumynin's study kept $\frac{m_s}{V}$ =0.1 g cm^{-3} and used a constant bulk density of 1.7 g cm^{-3}. To ensure that the inventory of Sr-90 was conserved in the system, $\frac{dM^T}{dt}$ was defined to be zero.

2.5 Biosorbent studies

A. Ahmadpour's study investigated the adsorption capacity of strontium ions onto almond hulls particles in an aqueous solution. The initial strontium was placed in an aqueous solution at concentrations of 45 mg L^{-1}. 0.3 g of almond hull sorbent were then added to 50 mL of the strontium solution. The samples were heated to 10, 25 and 45°C. For this thesis, only the results from 25 °C were considered because they were most consistent with the environmental variables in the dual site one component model. The samples were agitated and then analyzed at specified time points via atomic absorption spectrophotometry.

The adsorption percentage was determined by taking the difference between the initial and final concentrations. Similar to the Rumynin study, the adsorption isotherms were modeled, and the kinetics fit to rate equations explained in Section 4.1. The study found that green almond hulls achieved an adsorption capacity of 7 mg g^{-1} of strontium per gram of adsorbent at a temperature of 25 °C.

The adsorption kinetics of Sr-90 were best fitted as a first order quadratic rate equation as follows:

$$\frac{dS}{dt} = k_{ads}(q_e - S(t))^2 \qquad \textbf{(10)}$$

Where:

$S(t)$ is the concentration of Sr-90 per gram of the adsorbent at time t (mg g^{-1})

k_{ads} is the first order rate constant (g mg^{-1} min^{-1})

q_e is the adsorption capacity of strontium in the almond hull (mg g^{-1})

Table 3 presents the parameters defining the kinetics of almond hull on the injection solution at 25°C:

Table 3: Parameters to fit almond hull kinetics using 45 mg/L of strontium in solution with 0.3 g of biosorbent at a temperature of 25°C

Variable	Published Value	Unit
k_{ads}	0.80	g mg^{-1} min^{-1}
q_e	7.00	mg g^{-1}

CHAPTER 3- MATERIALS AND METHODS

3.1 Combining Models

The purpose of this thesis is to integrate a biosorbent model into Rumynin's dual-site-one-component model. The almond hull is treated as a third compartment that will compete for the adsorption of Sr-90. Both the almond hull model and the dual-site one component model are defined by first order rate equations discussed in the literature review. Both of the rate equations for the fluid activity concentration are combined and modeled using Euler's Method as described in the following sections.

The two rate equations for each rock type (Equations 5 and 6) need to be expressed as one rate equation for the injection solution $\frac{dC}{dt}$. The derivative of Rumynin's Mass Balance Equation (Equation 9) can be taken to solve for the $\frac{dC}{dt}$ term needed to solve for the system of differential equations. The method used to solve the differential equations is discussed further in Section 3.3. The first derivative of Rumynin's Mass Balance is taken to get:

$$\frac{dM^T}{dt} = \frac{VdC}{dt} + \frac{d}{dt}\left(\frac{m_s}{\rho_b} N\right) \qquad \textbf{(11)}$$

Then applying the relationship between the two rock types:

$$\frac{dM^T}{dt} = 0 = \frac{VdC}{dt} + \frac{m_s}{\rho_b}\left[f\frac{dN_1}{dt} + (1-f)\frac{dN_2}{dt}\right] \qquad \textbf{(12)}$$

And solving for $\frac{dC}{dt}$:

$$\frac{dC}{dt} = \frac{-m_s}{\rho_b V}\left[f\frac{dN_1}{dt} + (1-f)\frac{dN_2}{dt}\right] \qquad \textbf{(13)}$$

At this point, we can insert the sorbent (equation 10) into the system we arrive at:

$$\frac{dC}{dt} = \frac{-m_s}{\rho_b V}\left[f\frac{dN_1}{dt} + (1-f)\frac{dN_2}{dt}\right] - \frac{dS}{dt} \qquad \textbf{(14)}$$

The units in the original $\frac{dS}{dt}$ equation need to be converted to units of Bq cm^{-3} such that it can be directly inserted into the $\frac{dC}{dt}$ equation. Adhmadpour's variables were presented in units of mg g^{-1}, mg of strontium per gram of sorbent. The adsorption constants were converted to cm^3 Bq^{-1} d^{-1} and Bq cm^{-3} for k_{ads} and q_e respectively. The units must be consistent across all of the equations to merge the two models together.

The unit conversion uses the following justifications:

1. The study used 0.2 g of almond hull sorbent per 50mL of flushing solution.
2. The specific activity for Strontium 90 is 5.21E+12 Bq g^{-1}

Below is the conversion for the $q_e$variable

$$x\left(\frac{mg}{g}\right) * \frac{0.2\ g}{50\ ml} * 5.21 * 10^9\left(\frac{Bq}{mg}\right)\left(\frac{1m\ l}{1cm^3}\right) = x\left(\frac{Bq}{cm^3}\right) \qquad \textbf{(15)}$$

The same conversion can inversely apply for k_{ads} also including time.

Below is a table of the published rate constants and the unit converted constants for implementation into the dual-site-model. The model fits the experimental data with an R^2 value of 0.99.

Table 4: Published Sorption Kinetic Constants vs Converted

Variable	Published Value	Unit	Converted Value	Unit
k_{ads}	0.80	g mg^{-1} min^{-1}	5.53E-5	cm^3 Bq^{-1} d^{-1}
q_e	7.00	mg g^{-1}	1.46E+08	Bq cm^{-3}

Table 3 presents of all parameters used in the experiment:

Table 5: Sorption Kinetic Constants for Biosorbent, Rock Type 1, and Rock Type 2

Parameter	Value	Unit
f	0.75	-
α_1	60	d^{-1}
α_2	60	d^{-1}
K_{F_1}	10	$(\mathrm{Bq}\ cm^{-3})^{1-n_1}$
K_{F_2}	532	$(\mathrm{Bq}\ cm^{-3})^{1-n_2}$
n_1	1.03	-
n_2	1.03	-
$\frac{m_s}{V}$	0.1	$(\mathrm{Bq}\ cm^{-3})$
ρ_b	2.6	$\mathrm{g}\ cm^{-3}$
k_{ads}	5.53E-5	$g\ Bq^{-1}\ d^{-1}$
q_e	1.46E+08	$Bq\ cm^{-3}$

3.2 Considerations

There are several factors that need to be considered when combining the two adsorption models. The environmental parameters and initial conditions need to be consistent.

Adhmadpour's study used the mass concentration as the unit of measurement for strontium, not the activity concentration. These need to be converted into units of activity concentration. If the strontium isotope was pure radioactive Sr-90, it would convert to 2.34E+08 Bq cm^{-3}. This is within one order of magnitude of the highest initial concentration of strontium in the Rumynin study, 1.62E+07 Bq cm^{-3}. Ahmadpour's study only investigated two fluid concentrations with varying kinetic parameters. The dual-site-one-component model for Strontium 90 accurately models the kinetics for five different concentrations across five different orders of magnitude. The composite model assumes that the model will fit an initial concentration of 2.34E+08 Bq cm^{-3} so that the almond hull model will work as designed.

The environmental parameters from each experiment need to be relatively consistent between the two models.

- The almond hull experiment was conducted at 25 °C while the Rumynin study conducted their batch experiments at 20°C.
- Both experiments were also conducted at atmospheric pressure.

Given the similarities, both experiments should be able to be combined to explore the three-part sorption competition: Rock Type 1, Rock Type 2, and the biosorbent.

3.2 Solving Differential Equations

Rumynin's study used numerical algorithm to solve for adsorption curves over time. There were no details published on the exact software or script used to solve for certain parameters in the model. The composite model will use two different methods to solve for the system of differential equations: Euler's Method and the Anylogic software package. The fundamental theories are presented in section 3.3.

3.3 Euler's Method

Euler's method is used to approximate solutions to first order differential equations. We are using this as a numerical integration technique for estimating the solutions to this system of differential equations. As an example, suppose that we are given the following:

$$\frac{dy}{dt} = f(x, y)$$

$$y(x_o) = y_o$$

Where f(x, y) is a known function and y_o is a known initial value. We want to solve for y(x). Therefore, the point (x_o, y_o) is an exact value known to lie on the solution curve. Then, at some arbitrary value of x:

$$y = y_o + f(x_o, y_o)(x - x_o)$$

If the difference between $x=x_1$ and x_o is small enough, then the point $y=y_1$ on the tangent line should be a close approximation of the actual value of the solution $y(x_1)$. Therefore:

$$y_1 = y_o + f(x_o, y_o)(x_1 - x_o)$$

To solve for y_1, the same principal can be applied.

$$y_2 = y_1 + f(x_1, y_1)(x_2 - x_1)$$

Where y_1 and $f(x_1, y_1)$ are already known quantities. Assuming that the difference between each consecutive x value is equal to h, then a recursive formula is produced:

$$x_{n+1} = x_n + h$$

$$y_{n+1} = y_n + h * f(x_n, y_n)$$

The smaller the value of h, the better the approximation of y. (Davis, 1984)

3.4 Anylogic

The Anylogic tool uses object-oriented system dynamics to solve systems of equations. The user can visually relate stocks and flows to simulate a system. The stocks define the initial conditions of each parameter in a system whereas the flows represent the rate equations governing the interactions between the stocks. The system of stocks and flows are governed by feedback loops to numerically solve the differential equations. These stocks and flows are displayed visually on the graphic user interface such that each dependency can be mapped. Once the system is mapped and the dependencies defined, Anylogic runs an Euler Approximation to calculate the best result. Figure 4 illustrates the user interface to define stocks and flows.

Figure 4: Simple system of one stock and two flows as shown on the Anylogic graphic user interface

CHAPTER 4 – RESULTS

4.1 Kinetics of Rumynin's Model

In this study, Rumynin's differential equations were solved using two different methods: an AnyLogic systems dynamic model and a numerical integration using Euler's method. Both methods produced identical results but did not match the batch data results. The activity concentration in the injection solution dropped far too rapidly. In the dual-site-one-component adsorption model, the only time-dependent parameter is the kinetic Freundlich constant. A correction factor can be applied to Kinetic Freundlich Constant to slow down the interaction. This correction factor can be applied as a new parameter and then optimized to best fit Rumynin's batch data. This correction factor applies to the alphas as shown in Table 3. In order to model the batch data using the Rumynin equations 1 and 2, the alphas must be divided by 2547 as the correction factor. This value was calculated using Microsoft Excel's Solver Function to minimize the difference between the simulation and Rumynin's batch data. With this correction factor, Rumynin's results as concentrations vs. time in his paper are matched. Therefore, we will use the Rumynin equations with the constants from Table 3, except for dividing the alpha by 2547.

Figure 4 below shows comparisons to what the Rumynin model produces vs. what the current model produces. Both approach the same asymptotic value, describing equivalent equilibrium conditions. As can be seen, the current model fits the batch data as well as what is supplied in the Rumynin paper:

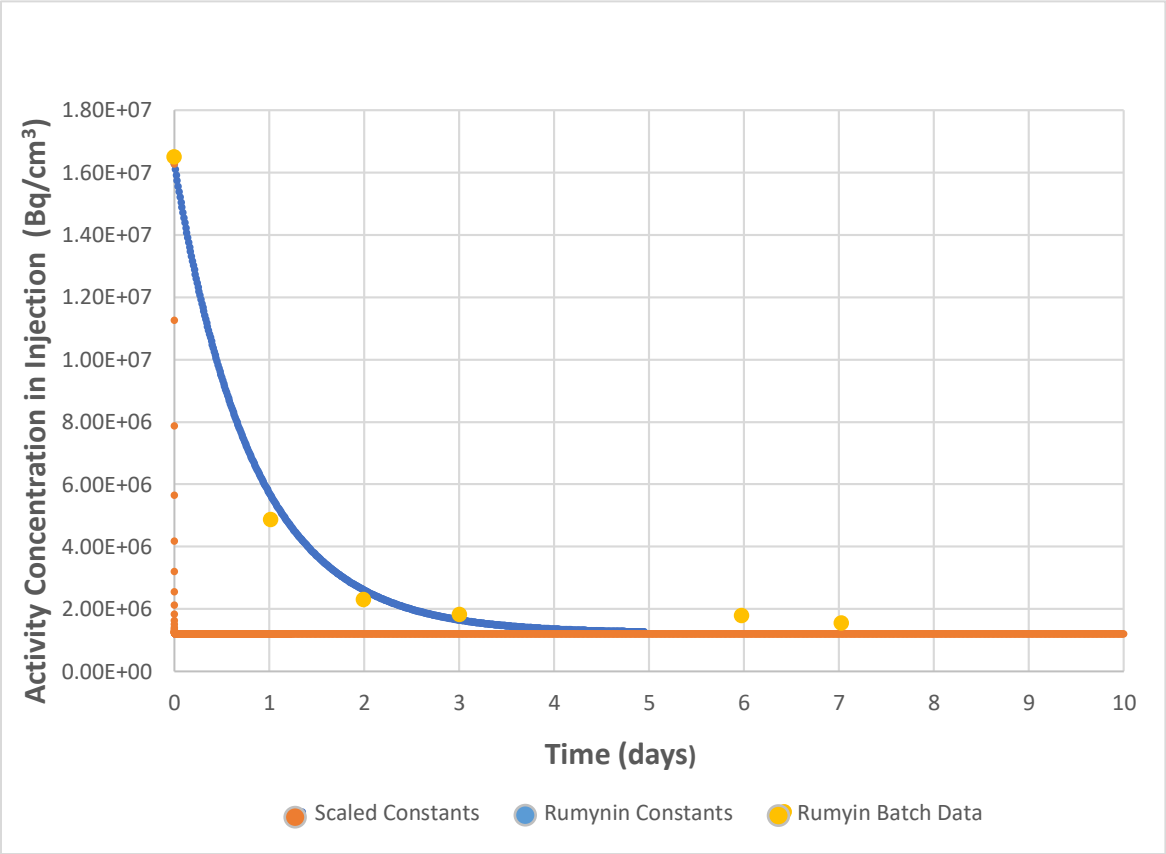

Figure 5: Activity Concentration of the Injection fluid for Rumynin's Published Batch Data and Simulations using the Published Constants and the Scaled Constants

Rumynin's model demonstrates a decline in the activity concentration in the injection solution due to the adsorption from the rock. Rumynin's study only qualitatively described the rock kinetics. Figure 5 is a graph showing the activity concentrations in both types of rock:

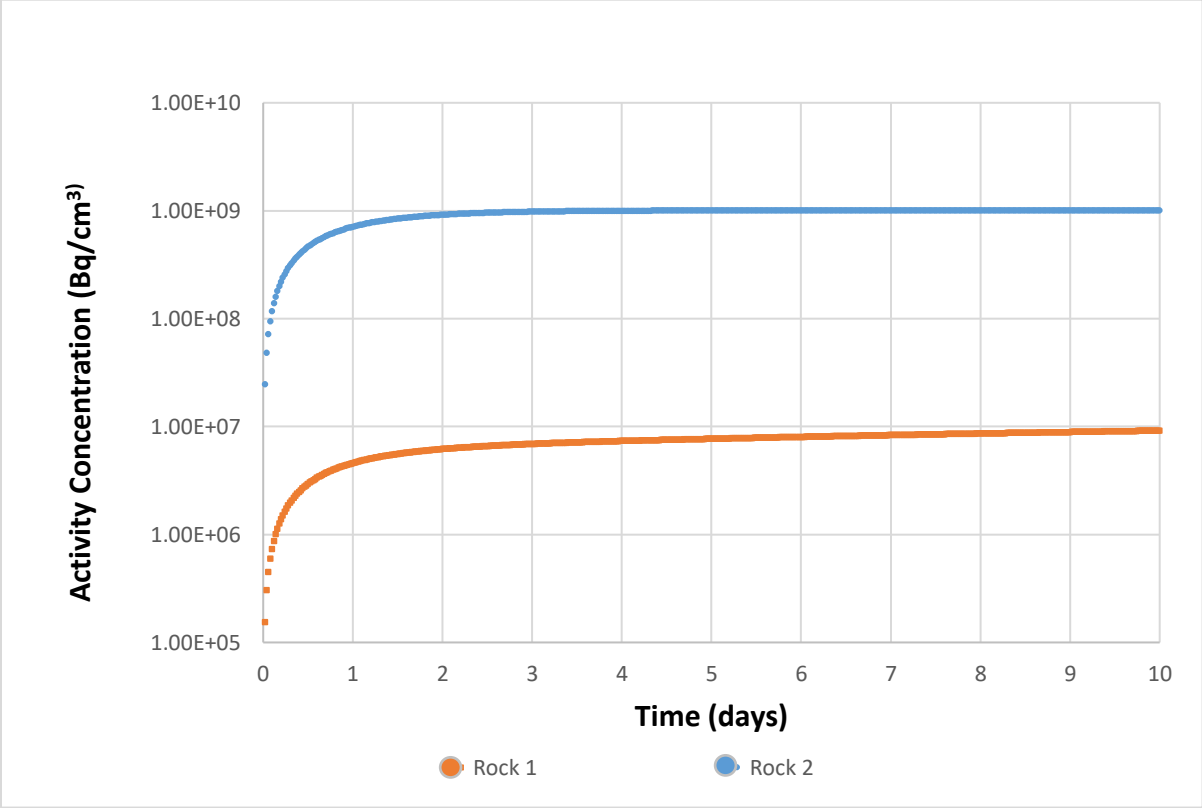

Figure 6: Activity Concentration in Rock Type 1 and Rock Type 2

The activity concentration resulted in 9.97E+08 Bq/cm^3 in Rock Type 2 and 9.08E6 Bq/cm^3 in Rocky Type 1. The higher Linear Freundlich Constant from Rock Type 2 leads to much more Sr-90 adsorption than Rock Type 1. The difference in Linear Freundlich Constants results in over 100 times more Sr-90 being adsorbed into Rock Type 2 than Rock Type 1.

4.2 Introduction of Almond Sorbent

The introduction of an almond hull sorbent into the injection solution is characterized by a much a more rapid decline in activity concentration compared to an injection solution with no sorbent added. A comparison of the injection fluid with and without almond hull sorbent is shown in Figure 6:

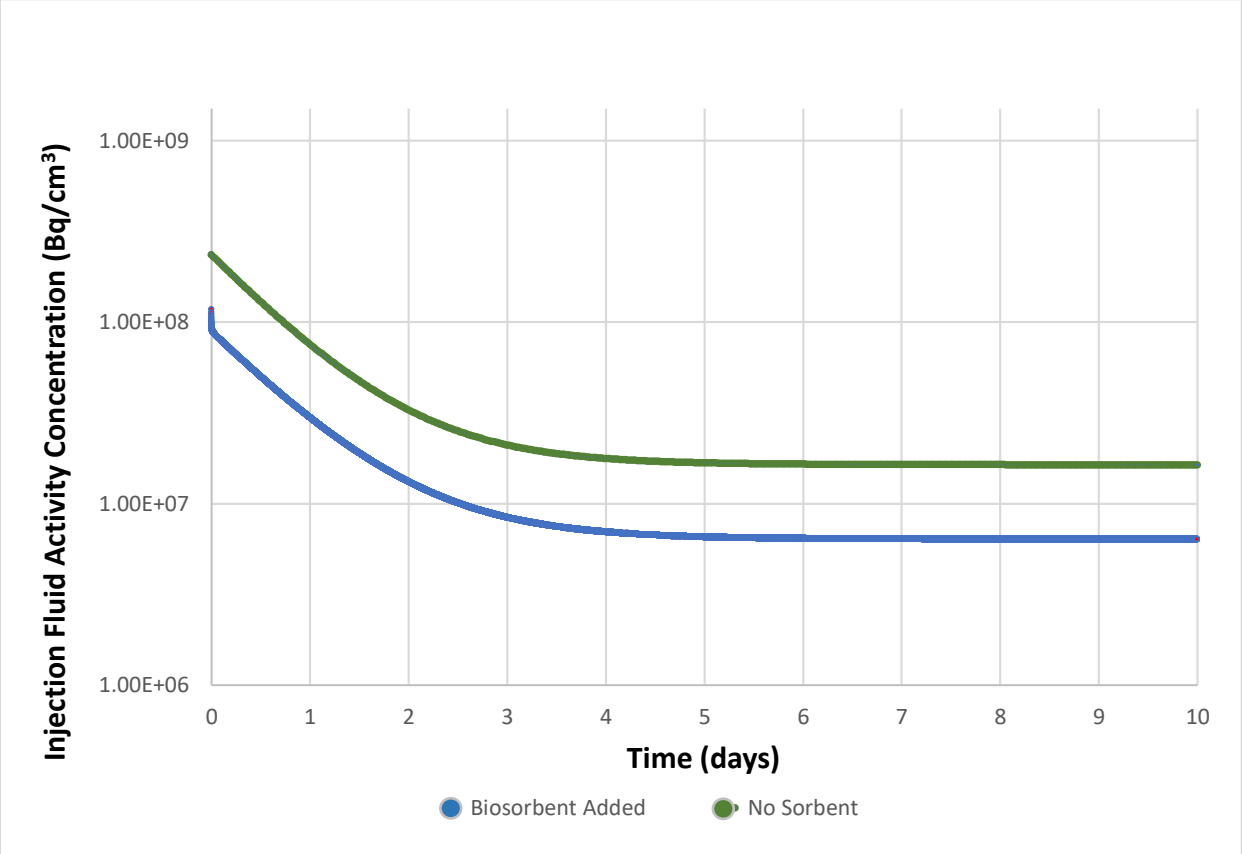

Figure 7: Activity Concentration of the Injection Fluid with Almond Hull Sorbent Compared to No Sorbent

The Ahmadpour study noted that most of the adsorption occurred in the first three minutes. The simulation is consistent with these findings. The sorbent in the system acts on a much faster time scale than the rock, adsorbing the Sr-90 almost immediately. With the sorbent, after 10 days the activity concentration in the injection solution was

6.36E+06 Bq/cm^3. With the biosorbent added, after 10 days the activity concentration in the injection solution is 39% of the activity concentration without. With the sorbent added, the activity concentration after 10 days is also 2.7% of the initial activity concentration before it was injected.

Once the almond hull reaches its adsorption capacity, the rock interactions begin to dominate the interactions. Rock Type 1 and Rock Type 2 now have less Sr-90 ions to adsorb, leading to much lower activity concentrations than without sorbent in the system.

Figure 7 depicts activity concentrations Rock Type 1 and Rock Type 2:

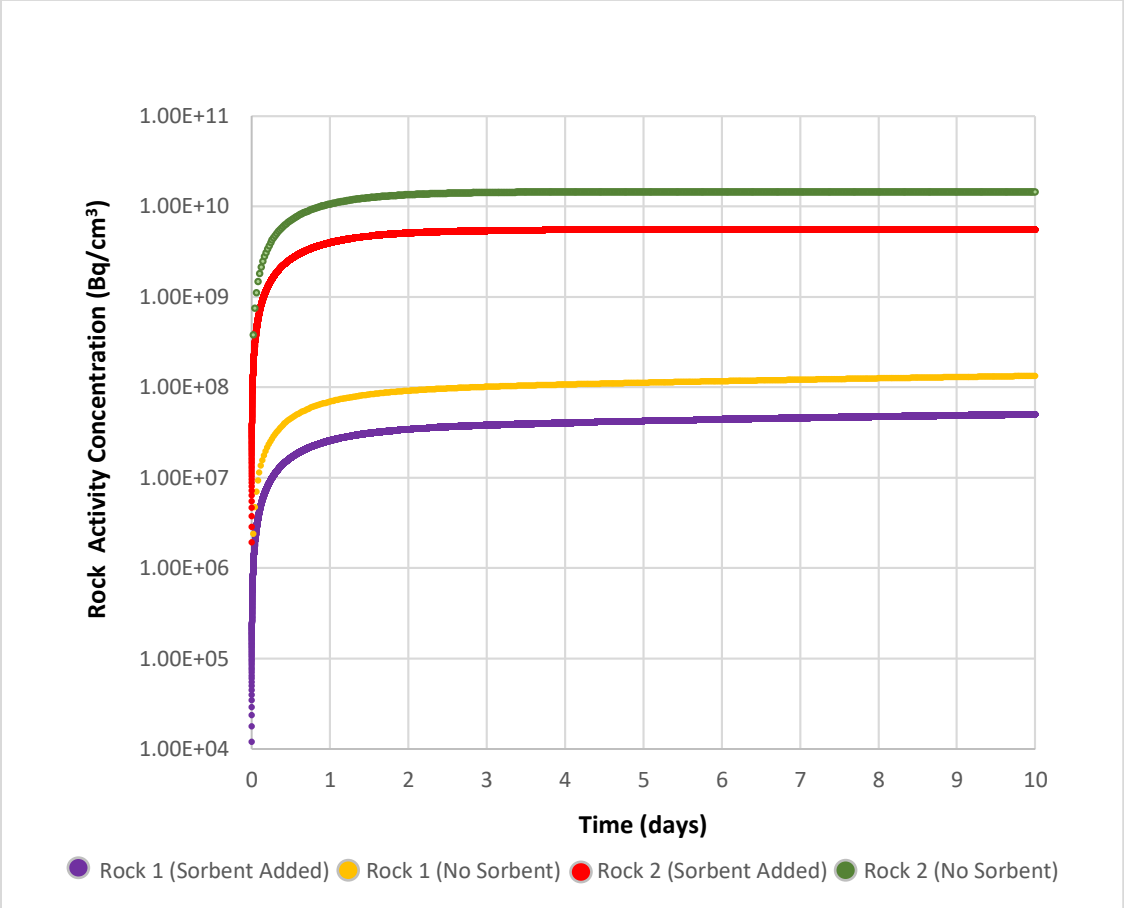

Figure 8: Activity Concentration in Both Rock Types, With and Without Sorbent

With the introduction of the almond hull sorbent and almost immediate adsorption, the aquifer rock has fewer Sr-90 ions in which to interact. This leads to less Sr-90 being adsorbed into both Rock Type 1 and Rock Type 2 compared to without any sorbent. For Rock Type 2, after 10 days, the activity concentrations were 1.45E+10 Bq/cm^3 without sorbent added and 5.46E+09 Bq/cm^3 with the sorbent added. The introduction of the almond hull biosorbent leads to an 62% decrease in the total activity concentration in Rock Type 1 after 10 days. A similar result is seen for Rock Type 2. After 10 days, the activity concentration was 1.30E+08 Bq/cm^3 without the sorbent added and 5.01E+07

Bq/cm^3 with the sorbent added. A similar 61% decrease in the activity concentration was also found for Rock Type 2. This implies that the almond hull sorbent effected both Rock Type 1 and Rock Type 2 equally.

The introduction of the almond hull affecting both compartments equally is hypothesized to be due to the time-frames in which the compartments interact. The almond hull acheives saturation almonds immediately with the adsorption rate dropping to near zero. Once the almond hull achieves saturation, the dual-site one-component model takes over. We see that the shape of the curves remain similar because the shape is attributed to the Exponential Freundlich Constant, which remains unchanged. There is no evidence to support that this would be the case in a batch experiment.

CHAPTER 5 – DISCUSSION

The purpose of this thesis is to address the question of whether a biosorbent within the injection could immobilize the Sr-90 ions therefore reducing the available Sr-90 ions for adsorption into the surrounding rock. The study did show that the activity concentration in the rock was reduced by 61-62% for both rock types. This is simply not enough for a remediation attempt using an initial activity concentration of 2.34E+08 Bq cm^3.

5.1 Implications

The model does show promise if lower activity concentrations are used. The equations for the biosorbent compartment show that the biosorbent asymptotically approaches a saturation activity concentration. Based solely on the equations, if the injection solution were to be less than this saturation concentration (1.46E+08 Bq/ cm^3), the biosorbent acts fast enough that there would be no ions available to the rock. When these parameters are inputted into the three-part model, the activity concentration in the injection solution compartment drops immediately to zero within the first 0.003 days. Ahmadpour's model was not designed for lower concentrations of strontium.

Further batch studies would be required for Sr-90 activity concentrations less than 2.34E+08 Bq/cm^3. Rumynin's experiment proved the model worked for concentrations ranging several orders of magnitude. Ahmadpour's experiment was more limited. Ahmadpour's study developed a model that functioned for two specific strontium concentrations. Depending on the amount of biosorbent in the system, the removal efficiency varied from 45% to 79% (Ahmadpour, 2010).

Future experiments could provide data for the removal efficiency at lower concentrations and answer the question of whether the biosorbent completely immobilized the Sr-90. Based upon the results from these models, if the Sr-90 was completely immobilized, the contaminated aquifer could be remediated through flushing without the fear of contamination of the aquifer rock.

5.2 Inconsistencies between the models

Another factor that needs to be considered is the pH of the injection solution. Ahmadpour investigated the effect of the almond hull on the injection solution. They began with initial solutions having a pH of 3, 6, and 10.8. The almond hull was added to the solution and left for 24 hours. It was found that every solution asymptotically approached a pH of 6 regardless of the initial pH. Rumynin's model used a pH of 3 for the initial injection solution.

Rumynin’s model used an initial pH of 3.05 to 3.20 during the adsorption phase. It is not precisely known how the adsorption dual site model would change with a pH of 6. Experiments have been shown that quartz’s (60% abundance in Rumynin’s aquifer) surface charge density increases as the pH of the aqueous solution it is in contact with increases (Kitamura A.). This increased surface charge increases the adsorption capacity therefore increasing the amount of strontium adsorbed in the quartz.

Papers investigating the rate of adsorption of strontium onto quartz as a function of pH were not found. Given the biosorbent reacted orders of magnitude faster than the surrounding rock, further investigation would be needed to determine exactly how the difference in pH would affect the sorption kinetics.

5.3 Broadening the Application

The dual-site one-component model was designed to simulate the adsorption kinetics for one aquifer in Western Siberia. This has a very limited scope with only a single application. The model was designed such that it divided the model into two compartments that related to the mineral's mass-exchange properties. This train of thought could be expanded to characterize the Freundlich kinetic parameters for each mineral type. Instead of breaking it into two rock types, the Freundlich parameters could be modeled based on mineral composition. It would be an ambitious endeavor, but a broad batch study could be conducted to define the Freundlich adsorption parameters for each mineral type. These could then be combined similar to Rumynin's method of modelling, except this would enable any injection well to be modeled as long as the average mineral composition is known.

5.4 Further Expansion of Model

The goal of creating a simulation is to model a system as accurately as possible. The dual-site one-component model only considers the rock types in the aquifer. This is an oversimplified model of a more complex system. A natural aquifer contains an entire ecosystem living within it that could potentially adsorb strontium. A more complete model would include a compartment for the natural biomass in the aquifer.

The biomass can be suspended in the water or coating the surface area of the rock as a biofilm (Donlan, 2002). The biomass suspended in the aquifer will be displaced as the injection solution replaces it, but the biofilm is a crucial factor.

The treatment of biomass in the aquifer can pose to be a complex task. The biofilms are considered heterogeneous in their spatial structures and the species composing the biofilm (Costerton, 2007). Biofilms have been modeled as individual spheres stacked onto one another. The individual-based modeling approach represents biofilms as hard-spherical particles that adhere to the surface of the rock. The growth and movement of the particles of biofilm are determined by a set of rules depending on the local environment, such as the availability of nutrients and space (Kreft, 2001).

This model would require spatial modeling of the aquifer to estimate the available space and environmental sampling to determine the nutrient availability. This would expand the scope past a simple adsorption model and open the door for visual modeling of the system.

CHAPTER 6 – CONCLUSION

This study explores a potential technique to reduce the amount of radioactive strontium-90 adsorbed into a contaminated aquifer. It models the competitive process between the adsorption of Sr-90 from the surrounding rock and the newly introduced biosorbent. The thesis addresses the question of whether a biosorbent within the injection could immobilize the Sr-90 ions therefore reducing the available Sr-90 ions for adsorption. The results from this study support the claim that the biosorbent could be used to immobilize the Sr-90 ions, limiting the amount adsorbed into the surrounding rock. The experiment discovered:

- With the biosorbent added to the injection solution, the activity concentration in both rock types was 61-62% lower than without any sorbent in the system.
- With the biosorbent added, the activity concentration in the injection solution is 39% of the activity concentration without after 10 days.
- With the sorbent added, the activity concentration after 10 days is also 2.7% of the initial activity concentration (t=0).
- The model indicates that if the almond hull adsorbent was introduced to an injection solution with an activity concentration lower than adsorption capacity of the adsorbent, all the Sr-90 would be immobilized.

Given the initial activity concentration of 2.34E+08 Bq cm^3, after 10 days, it still leaves a considerable amount of contamination in the aquifer. The biosorbent compartment of the model equations show that the almond hull rapidly approaches an adsorption

capacity. Further experiments could be conducted at lower activity concentrations to determine if this adsorption capacity is reached. The radioactive strontium would then be adsorbed onto the almond hull preventing adsorption into the aquifer rock. Batch experiments could then be conducted with a biosorbent to confirm such theories.

The implications of this model are promising, but further investigation needed to determine the accuracy of such a model. The composite model built in this study simulates the addition of a biosorbent into the injection fluid to compete with high/low relative surface area type minerals for the adsorption of radionuclides. This only simulated one part of the entire system. The biofilm living within the aquifer could be modeled as a separate compartment to compete for the adsorption of strontium. A more accurate model could provide industries with contaminant models to aid in remediation in case of a contaminated aquifer.

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